

How does confinement in nano-scale pores change the thermodynamic properties and the nature of phase transitions of water?

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We analyze thermodynamics of water samples confined in nanopores and prove that although the freezing temperature can be dramatically lower, the suppression of the ice nucleation leading to the freezing temperature depression is a truly macroscopic effect rather than a consequence of microscopic interactions. The freezing transition itself is a truly collective phenomenon described by a macroscopic order parameter (the nearly homogeneous density of the liquid within the pore away from the pores wall) exactly in the same way as in the bulk liquid. The thermodynamics properties of the confined and the bulk liquid can be described by macroscopic thermodynamics and be readily related to each other simply by proper inclusion of the additional Laplace pressure exerted by the solid-liquid boundary.

Liquid water confined in nanopores can be prevented from freezing well below the natural freezing point (see e.g. [1–5] and references therein). The appearance of the liquid water at such extremely low temperatures was often used to probe the properties of supercooled water experimentally. More recently the dielectric properties of the water samples in MCM-41 nanopores were studied within the temperature range corresponding to the λ -point of the bulk liquid [6, 7]. The observed λ -feature of the dielectric constant within the liquid phase of the sample is a signature of a ferroelectric phase and thus seem to confirm earlier theoretical predictions made for a bulk supercooled water [8]. The suggested relation brings up a natural criticism since there is no clear cut answer to the question up to a which point and how the properties of the confined water samples can be related to the properties of the bulk liquid? In particular how similar or how different are the phase transitions and thermodynamics properties of the confined and bulk liquid?

The question has a long history and a good summary on the existing views can be found in [9]. Indeed, once confined within a nano-scale pore a water sample does differ from a bulk liquid in a number of important ways:

- 1) the freezing temperature is dramatically lower (the so called freezing temperature depression phenomenon) and can be made as low as -100°C ;
- 2) the cooling/freezing cycle of the confined water shows hysteresis, i.e. the difference between the melting and the freezing temperatures in a single experiment as described in e.g. [1–4, 6, 10];
- 3) on top of that, the neutron scattering experiments combined with a number of Molecular Dynamics (MD) simulations [5, 11–19] show that the water molecules show complex distribution patterns and the (molecular)

density of liquid within the confined water samples is far from being homogeneous, which is characteristics of a bulk liquid.

On the other hand, as also highlighted in [9], the MD simulations of water interacting with a hydrophilic surfaces of e.g. silica-based nanopores such as MCM-41 show that the hydrophilic surfaces do not have serious effects on the properties of water, except for significantly lowering the freezing temperature and stabilizing the liquid phase [20, 21]. Similarly only negligible hysteresis was observed in the MCM-41 confined system by means of X-ray scattering and calorimetric experiment [3, 22]. In another example, the difference between melting and freezing temperatures is only $\Delta T_H \sim 1\text{K}$ in MCM-41 3.5nm -samples [4].

Here we revisit the arguments and show that in spite of the apparent differences the properties of the water samples confined in nanopores are extremely relevant for the comprehension of the low-temperature properties of the bulk water, especially if collective properties of the water samples are probed. In spite of the fact that the freezing temperature of the small samples can be made dramatically lower, the suppression of the ice nucleation leading to the freezing temperature depression is a truly macroscopic effect rather than a consequence of microscopic interactions. The freezing transition itself is a truly collective phenomenon described by a macroscopic order parameter characterizing the nearly homogeneous density of the liquid within the pore away from the pores wall. The thermodynamics properties of the confined and the bulk liquids are still macroscopic and can be immediately related to each other simply by proper inclusion of the additional Laplace pressure arising from the interaction with the pores walls.

To make the point let us carefully derive the freezing temperature depression ΔT_f using the macroscopic arguments only. Typical experimental system, e.g. MCM-41 (Mobile Crystalline Material) is a silicate obtained by a templating mechanism [23]. By changing the length of

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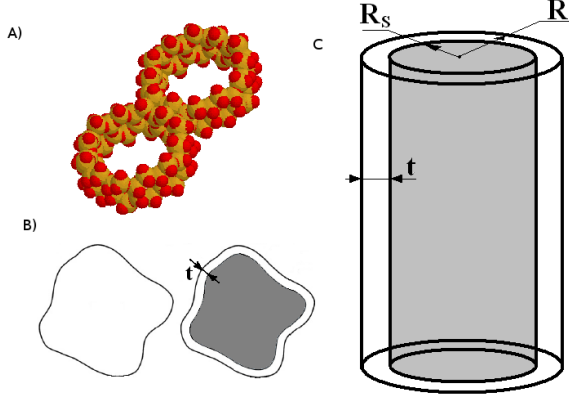


Figure 1: The 3D representation of the two cylindrical pores of MCM-41 (A). The schematic representation of a cross-section (B) of a water sample confined to a pore at two the temperatures above (left) and below the freezing point (right). The ice phase region is shown by gray, non-freezing layer is next to the pore wall. The idealized model (C) of a cylindrical pore (see the explanation in the text).

the template molecule, the width of the channels can be controlled to be within 2 to 10 nm. The walls of the channels are amorphous SiO_2 (see Figure 1A). To simplify the analysis we follow [4, 24] and consider a simple cylindrical pore of the length L and radius R filled by liquid water at sufficiently high temperature above the freezing transition first. As the temperature decreases there will be a growing body of ice within the pore. To model the appearance of the so-called “non-freezing layer” [2–4] let us assume the ice filling the coaxial cylinder of radius $R_S = R - t$, where $t \approx 0.4\text{nm}$ is the thickness of a narrow liquid layer next to the cylinder walls that does not freeze (see Figure 1B, C). Without loss of generality we further neglect the difference between the particle densities of the liquid and the solid states and assume $n_S = n_L$. Then at every specified value of pressure P each of the states of the liquid can be characterized by the corresponding chemical potentials (i.e. Gibbs energy per molecule), $\mu_L(P, T) \equiv \mu_L$ and $\mu_S(P, T) \equiv \mu_S$, respectively.

The liquid interacts with the ice body forming within the pore, which leads to the additional Laplace pressure, associated with the interface curvature: $\Delta P_L = \gamma_{SL}/R_S$, where $\gamma_{SL} = 32\text{erg/cm}^2$ is the surface tension coefficient characterizing the ice-liquid boundary [25]. Therefore the ice is additionally compressed by the Laplace pressure $P + \Delta P_L$. As the ice grows and the ice sample radius increases by dR_S , then the number of molecules in the solid phase increases by $dN = n_S \cdot 2\pi R_S dR_S$ molecules transferring from the liquid to the ice. Consequently the Gibbs energy of the system changes by $dG = dG_S + dG_L$, where $dG_S = \mu_S(P + \Delta P_L, T) dN$, and $dG_L = -dN \mu_L(P, T)$ are the Gibbs energy changes in each of the phases. Using Gibbs-Duhem relation, $d\mu_S = dP/n_S - s_S dT$, where s_S is the entropy per one molecule in the solid state, we

find that

$$dG_S \approx [\mu_S(P, T) + \delta\mu_S] dN,$$

where $\delta\mu_S = \Delta P_L/n_S$. Accordingly, the Gibbs energy of the ice sample formation can be obtained after integration of dG from $R_S = 0$ to its finite (current) value R_S :

$$\Delta G(R_S) = G(R_S) - G(0) = \Delta\mu \cdot n_S \pi R_S^2 L + 2\pi R_S L \gamma_{SL},$$

where $\Delta\mu = \mu_S - \mu_L$. Using the equilibrium condition $\Delta G = 0$ at $R_S = R - t$ we can establish the equilibrium freezing temperature, $T_f = T_\infty + \Delta T_f$, where T_∞ is the freezing temperature of the bulk liquid satisfying the equation $\Delta\mu_\infty = \mu_S(P, T_\infty) - \mu_L(P, T_\infty) = 0$. Since the freezing occurs at $P = \text{const}$, $\Delta\mu \approx \Delta\mu_\infty + \Delta T_f(s_L - s_S) = \Delta T_f \Delta h / T_\infty$, where Δh is the fusion enthalpy per one molecule and hence

$$\Delta T_f = -C / (R - t), \quad (1)$$

where $C = 2\gamma_{SL}T_\infty/\Delta h = 52.4\text{nm} \cdot K$, and $\Delta h = n_S \Delta h = 3.3 \cdot 10^9 \text{erg/cm}^3$. The result agrees well with the experimentally established values: $C = 52.4 \pm 0.6\text{nm} \cdot K$ [1], $C = 52 \pm 2\text{nm} \cdot K$ [3] (see [4] for a more complete list of experiments).

The very fact that the freezing temperature depression (1) can be reliably derived from the macroscopic thermodynamics arguments only is a good indication of the macroscopic nature of the freezing transition and the freezing depression phenomenon in water confined in rather wide pores ($R \gg t$) even at a very low temperature. The derivation shows that the freezing temperature depression (1) can be simply explained by the increase of the Gibbs energy of the ice by $\Delta G_S = V_S \Delta P_L = N_S \delta\mu_S$ due to the additional Laplace pressure ΔP_L exerted by the solid-liquid interface curvature.

Further analysis of the proposed derivation lets us to draw or to restate a number of important conclusions. First, the hysteresis phenomenon brought up in [9] to highlight the difference between the confined samples and the macroscopic liquid can be well explained within macroscopic thermodynamics as a consequence of the metastability of the liquid and solid phases in the course of a supercooling and/or super-heating experiments [2, 4, 26]. As in a ferromagnet, the difference between the freezing and the melting temperatures (the measure of the hysteresis) ΔT_H is determined by the value of the free energy barrier ΔG_B separating the molten and frozen states of the pore and as such depends on the specific path taken to overcome the barrier. According to our derivation the barrier height, $\Delta G_B = \pi\gamma_{SL}L(R - t)/2$, corresponds to the Gibbs energy of the half-frozen state of $R_S = (R - t)/2$. Note that because of the linear dependence of the barrier energy ΔG_B on the sample size L , in actual experiments the ice shows up in smaller pieces characterized by smaller values of L first.

Second, the freezing temperature of the whole sample is defined by the single free energy balance, $\Delta G = 0$. The molecular density of the water samples is practically homogeneous at $R \gg t$ and hence freezing occurs everywhere within the water sample at the same time at a single temperature. Therefore the freezing transition is a collective, cooperative phenomenon. This picture is supported by the molecular dynamics [21] simulations and means the water in sufficiently large pores is to a good degree a homogeneous liquid characterized by the bulk thermodynamic properties. This homogeneous density plays a role of the collective order parameter. Therefore the ice nucleation suppression in nanopores is not a microscopic, but rather a macroscopic effect. The inhomogeneous water density profile observed in the neutron scattering experiments does take place but apparently does not influence observable thermodynamic characteristics. These arguments have a general character and hold, for example, for melting of nm-sized crystalline solid particles [27, 28] and the derivation of Kelvin equation for the pressure of vapor in equilibrium with liquid droplets [29]. In each of the cases the thermodynamics properties of the infinite (bulk) medium were successfully used to describe the properties of nm-sized particles. The similarity makes us expect that freezing phase transition of

confined water in the pores should be smeared-out in the PT plane due to essential fluctuations related to the finite number of molecules in pores.

We presented a line of arguments to support the collective nature of the phase transitions and a deep relation between the bulk and confined liquid properties as soon as the water samples contained in nanopores of sufficiently large radii, $R \gg t$. One of the recent examples concerns the measurements of the dielectric properties of liquid water confined in MCM-41 nanopores of $D = 3.5\text{nm}$ size and thus prevented from freezing well below the natural freezing point at temperatures roughly corresponding to the so called λ -point first observed in the bulk water [30]. The dielectric constant of the water samples manifests a profound bump in the dielectric constant rising from the typical value $\epsilon \sim 10^2$ to as much as $\epsilon \sim 2 \cdot 10^4$ within the narrow temperature range $\Delta T \sim 1\text{K}$ near $T_F^{exp} \approx 235\text{K}$ in the liquid phase [6, 7] in accordance with the earlier theoretical predictions [8]. Since the dielectric susceptibility increase is a signature of a ferroelectric phase [31] and the ferroelectric ordering is a collective phenomenon, we can argue that ferroelectric features observed in nanopores do occur and should be eventually observed in the bulk liquid water near the λ -point.

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- [1] S. Jähnert, F. Chávez, G. Schaumann, A. Schreiber, M. Schönhoff, and G. Findenegg, *Phys. Chem. Chem. Phys.* **10**, 6039 (2008)
 - [2] K. Morishige and K. Kawano, *The Journal of chemical physics* **110**, 4867 (1999)
 - [3] A. Schreiber, I. Ketelsen, and G. Findenegg, *Physical Chemistry Chemical Physics* **3**, 1185 (2001)
 - [4] O. Petrov and I. Furó, *Prog Nucl Magn Reson Spectrosc* **54**, 97 (2009)
 - [5] M. Mazza, K. Stokely, E. Strelakova, H. Stanley, and G. Franzese, *Computer Physics Communications* **180**, 497 (2009)
 - [6] G. Bordonskiy, A. Gurulev, A. Orlov, and K. Schegrina, *Arxiv preprint arXiv:1204.6401*(2012)
 - [7] P. Fedichev, L. Menshikov, G. Bordonskiy, and A. Orlov, *JETP Letters* **94**, 401 (2011), *arxiv preprint arXiv:1104.1417*
 - [8] L. Menshikov and P. Fedichev, *Russian Journal of Physical Chemistry A, Focus on Chemistry* **85**, 906 (2011), *arXiv:0808.0991*
 - [9] H. Stanley, S. Buldyrev, P. Kumar, F. Mallamace, M. Mazza, K. Stokely, L. Xu, and G. Franzese, *Journal of Non-Crystalline Solids* **357**, 629 (2011)
 - [10] G. Findenegg, S. Jähnert, D. Akcakayiran, and A. Schreiber, *ChemPhysChem* **9**, 2651 (2008)
 - [11] D. Steytler and J. Dore, *Molecular Physics* **56**, 1001 (1985), ISSN 0026-8976
 - [12] M. Bellissent-Funel, J. Lal, and L. Bosio, *The Journal of chemical physics* **98**, 4246 (1993), ISSN 0021-9606
 - [13] T. Takamuku, M. Yamagami, H. Wakita, Y. Masuda, and T. Yamaguchi, *The Journal of Physical Chemistry B* **101**, 5730 (1997), ISSN 1520-6106
 - [14] R. Mancinelli, F. Bruni, and M. Ricci, *Journal of Molecular Liquids* **159**, 42 (2011)
 - [15] M. Ricci, F. Bruni, and A. Giuliani, *Faraday Discuss.* **141**, 347 (2008)
 - [16] F. Bruni, M. Ricci, and A. Soper, *The Journal of chemical physics* **109**, 1478 (1998)
 - [17] D. Awschalom and J. Warnock, *Physical Review B* **35**, 6779 (1987)
 - [18] I. Brovchenko and A. Oleinikova, *ChemPhysChem* **9**, 2660 (2008)
 - [19] R. Mancinelli, F. Bruni, and M. Ricci, *The Journal of Physical Chemistry Letters* **1**, 1277 (2010)
 - [20] N. Giovambattista, P. Rossky, and P. Debenedetti, *Physical Review E* **73**, 041604 (2006)
 - [21] P. Gallo, M. Rovere, and S. Chen, *The Journal of Physical Chemistry Letters* **1**, 729 (2010)
 - [22] K. Morishige and K. Nobuoka, *The Journal of chemical physics* **107**, 6965 (1997)
 - [23] C. Kresge, M. Leonowicz, W. Roth, J. Vartuli, and J. Beck, *nature* **359**, 710 (1992)
 - [24] C. Faivre, D. Bellet, and G. Dolino, *The European Physical Journal B-Condensed Matter and Complex Systems* **7**, 19 (1999)
 - [25] W. Hillig, *Journal of crystal growth* **183**, 463 (1998)
 - [26] M. Shimoda, T. Mizusaki, M. Hiroi, A. Hirai, and K. Eguchi, *Journal of low temperature physics* **64**, 285 (1986)
 - [27] P. Couchman and W. Jesser, *Thermodynamic theory of size dependence of melting temperature in metals* (Nature Publishing Group, 1977)
 - [28] Q. Mei and K. Lu, *Progress in materials science* **52**, 1175 (2007)

- [29] L. Landau and E. Lifshitz, Course of Theoretical Physics **5** (1980)
- [30] I. Hodge and C. Angell, The Journal of Chemical Physics **68**, 1363 (1978)
- [31] H. Frohlich, *Theory of dielectrics: dielectric constant and dielectric loss* (Clarendon press Oxford, 1949)